Emissions Control for Lean Gasoline Engines

Jim Parks (PI), Todd Toops, Josh Pihl, Vitaly Prikhodko

Oak Ridge National Laboratory

Sponsors: Gurpreet Singh, Ken Howden, and Leo Breton

Advanced Combustion Engines Program
U.S. Department of Energy

ACE033
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Project Overview

Timeline

- Project began in FY12
- Project ongoing with annual goals through 2017

Barriers Addressed

- Barriers listed in VT Program Multi-Year Program Plan 2011-2015:
  - 2.3.1B: *Lack of cost-effective emission control*
  - 2.3.1C: *Lack of modeling capability for combustion and emission control*
  - 2.3.1.D: *Emissions control durability*

Budget

- FY15: $377k
- FY14: $400k
- FY13: $500k

Collaborators & Partners

- General Motors
- Umicore
- University of South Carolina
- University of Wisconsin
- Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS)

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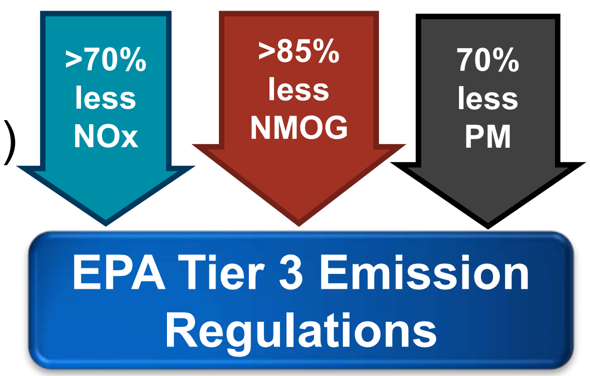
Objectives and Relevance

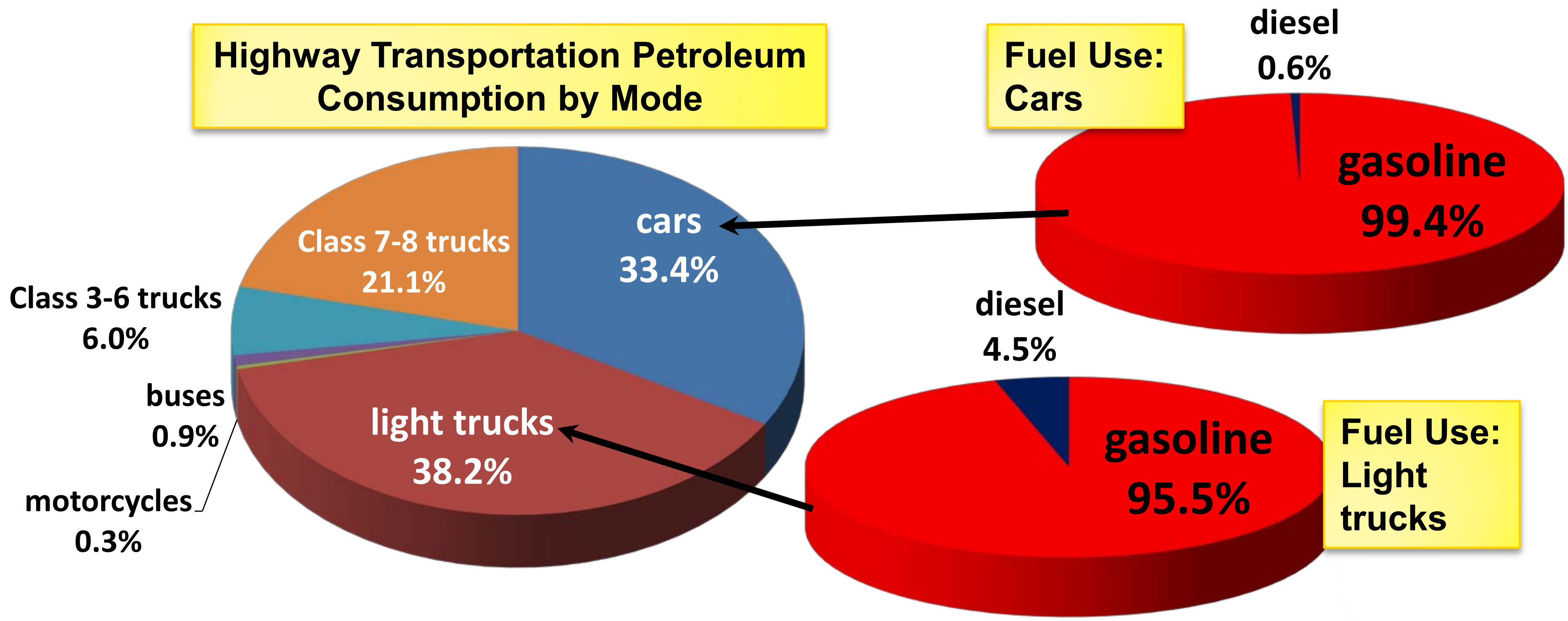
Enabling lean-gasoline vehicles to meet emissions regulations will achieve significant reduction in petroleum use

- Objective:
  - Demonstrate technical path to emission compliance that would allow the implementation of lean gasoline vehicles in the U.S. market.
    - Lean vehicles offer 5–15% increased efficiency over stoichiometric-operated gasoline vehicles
    - Compliance: U.S. EPA Tier 3 (originally Tier 2 Bin 2)
  - Investigate strategies for cost-effective compliance
    - minimize precious metal content while maximizing fuel economy



- Relevance:
  - U.S. passenger car fleet is dominated by gasoline-fueled vehicles.
  - Enabling introduction of more efficient lean gasoline engines can provide significant reductions in overall petroleum use
    - thereby lowering dependence on foreign oil and reducing greenhouse gases

Relevance: small improvements in gasoline fuel economy <u>significantly</u> decreases fuel consumption



- US car and light-truck fleet dominated by gasoline engines
- 10% fuel economy benefit has significant impact
  - Potential to save 13 billion gallons gasoline annually
- HOWEVER…emissions compliance needed!!!

Lean gasoline vehicles can decrease US gasoline consumption by <u>~13 billion gal/year</u>

References: Transportation Energy Data Book, Ed. 33 (2012 petroleum/fuel use data)

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Milestones and Project Goals

- Complete — **FY2014, Q1:** Measure transient NH_3 formed from TWC in an TWC+SCR approach on engine
- Complete — **FY2014, Q2:** Characterize performance of Umicore prototype TWC catalysts for NH_3 production
- Complete — **FY2014, Q3:** Present results at CLEERS Workshop
- Complete — **FY2014, Q4:** Define the potential impact of NOx storage components added to TWC formulations on NH_3 production for downstream NOx reduction over SCR catalysts
- Complete — **FY2015, Q2 [SMART]:** Determine effect of aging and/or poisoning on TWC NH_3 formation through flow reactor experiments *Further studies ongoing*
- On Track — **FY2015, Q4:** Simulate transient load/speed operation of passive SCR on BMW lean gasoline engine platform *Further studies ongoing*

In addition to milestones, a set of project goals has been adopted to ensure progression towards goal of low-cost emissions control solution for fuel efficient lean-burn gasoline vehicles

	FY13	*FY14*	*FY15*	*FY16*	*FY17*
Fuel economy gain over stoichiometric	7%	10%	10%	12%	15%
Total emissions control devices Pt* (g/L_{engine})	8	7	6	5	4

	5-year Average ($/troy oz.)	Pt-equivalent
Platinum	$ 1,504 /troy oz.	1.0
Palladium	$ 463 /troy oz.	0.3
Rhodium	$ 3,582 /troy oz.	2.4
Gold	$ 989 /troy oz.	0.7

* - will use Pt equivalent cost to account for different costs of Pt, Pd and Rh; 5-year average value fixed at beginning of project

Approach focuses on catalyst and system optimization of Passive SCR (and LNT+SCR)

Key Principle: system fuel efficiency gain depends on optimizing NH_3 production during rich operation and NOx reduction during lean operation

Minimize rich period of lean-rich cycle

Lean

Minimize engine out Lean NOx emissions

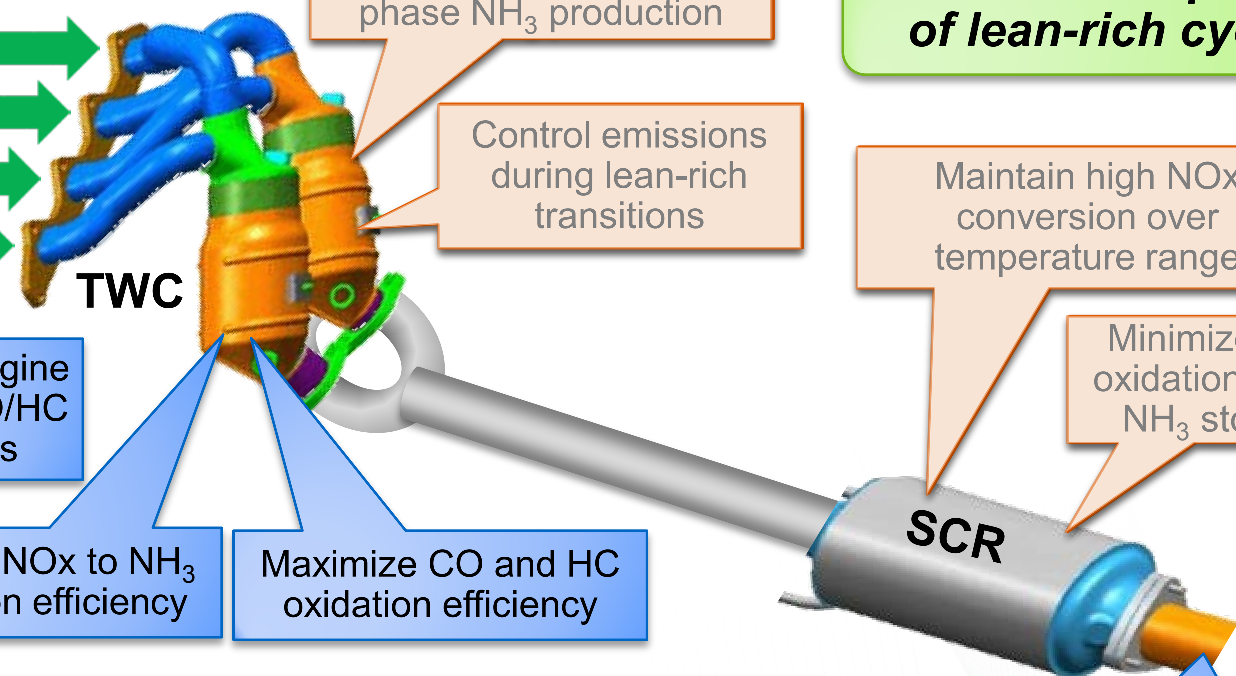
Lean Gasoline Engine

Add NOx storage for lean NOx storage and rich phase NH_3 production

Control emissions during lean-rich transitions

Maintain high NOx conversion over temperature range

Minimize NH_3 oxidation (keep NH_3 stored)



Maximize engine out Rich NOx emissions

Minimize engine out Rich CO/HC emissions

Rich

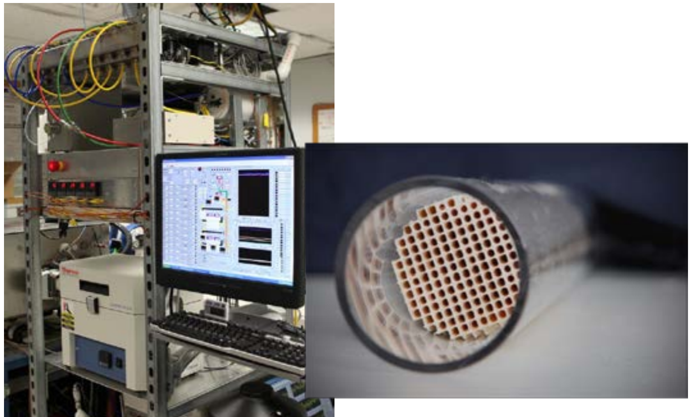
Maximize NOx to NH_3 conversion efficiency

Maximize CO and HC oxidation efficiency

Clean up CO/HC emissions (if needed)

Other Core Principles:
- Expand range of temperature operation
- Materials must be durable to temperature and poisons (S)
- Understand Pt group metals utilization to minimize cost

Iterative Bench Reactor + Engine Study Approach



Bench Flow Reactor with cycling and multi-catalyst (close-coupled and underfloor) capabilities

BMW 120i lean gasoline engine platform with National Instruments (Drivven) open controller

Define exhaust conditions

Formulation-dependent TWC performance

TWC performance vs. AFR with realistic HC and H_2 characterization

Controlled TWC+SCR system performance

Realistic TWC+SCR system performance with fuel efficiency measurement

TWC+SCR performance with refined load step cycle

Combustion parameter optimization to maximize NH_3 production

GM

System study guidance

umicore Automotive Catalysts

Prototype catalysts

Collaborations with modeling community and CLEERS

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Collaborations and Partners

Primary Project Partners

- **GM**
  - guidance and advice on lean gasoline systems via monthly teleconferences
- **Umicore**
  - guidance (via monthly teleconferences) and catalysts for studies (both commercial and prototype formulations)
- **University of South Carolina (Oleg Alexeev, Anton Lauterbach)**
  - Catalyst aging studies with student Calvin Thomas
- **University of Wisconsin (Chris Rutland)**
  - modeling of lean emission control systems

Additional Collaborators

- **CDTi**
  - catalysts for studies
- **CLEERS**
  - Share results/data and identify research needs
- **LANL**
  - Engine platform used for NH_3 sensor study (see LANL AMR talk ACE079)
- **MECA**
  - GPF studies via Work For Others contract
- **DOE VTO Fuel and Lubricant Technology Program**
  - Engine platform used for ethanol-based HC-SCR studies (see AMR talk FT007 - Todd Toops)

Responses to 2014 Reviewers

FY2014 AMR Review
(5 Reviewers)
[scores: 1 (min) to 4 (max)]

Category	Score
Approach	3.80
Tech Accomplishments	3.50
Collaboration	3.70
Future Research	3.60
Weighted Average	**3.61**

Approach: investigating alternatives to urea injection highly appropriate...low temperature limitations of urea based systems are a well-established barrier…nice evolution of understanding and following adjustment of approach…**using EGR and other engine means to adjust NOx and potential H_2 and/or NH_3 production is needed**... thorough job in devising a strong framework for the project

Technical Accomplishments: excellent outcome and worthwhile results…large amount of fundamental data displayed here was quite impressive…data appeared robust, **but more may be needed in the regards, e.g., repeatability, aging, poisoning effects**…**investigate novel purge strategies to limit CO production during the rich purges**…good correlation between laboratory results and vehicle…**DeSOx strategies were critical to enabling this technology to proceed and effect of SO_2/SO_3 on both the LNT and SCR**

Collaborations: excellent inclusion of both suppliers and OEMs…team was extremely strong…impressive

Future plans: **anxious to see the aging data**…combined TWC/NSC may be important enablers for meeting LEVIII and Tier II Bin 2 standards for lean systems…mixed thoughts on whether to focus on transients versus other key engine drivers like EGR or other engine calibrations…EGR understanding might be better to develop earlier, unless one sees more interesting transient results that can significantly impact the after-treatment fundamentals…**need to include purge strategy to limit impact of the rich purges on CO, HC, and fuel** economy…**important to better understand the PM and HC emissions on the vehicle**…keep an eye on N_2O

Relevance: 5-10% fuel consumption savings in the 2020 timeframe may cost OEMs about $75 per percent, leaves $500 added cost to a lean burn versus a stoichiometric GDI engine, **seems achievable**…running lean enhancements…**well focused on fuel economy targets**.

Funding: if more funds needed to shift some work into the engine approaches, money should be made available, at least enough to get data for a new proposal…**not sure why modeling had not been integrated into the tasks**

Responses to 2014 Reviewers

FY2014 AMR Review
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Approach: investigating alternatives to urea injection highly appropriate...low temperature limitations of urea based systems are a well-established barrier…nice evolution of understanding and following adjustment of approach…

Comment Area	Response
Reviewers complemented approach and accomplishments	Continuing approach and targeting project goals
Combustion parameters for optimal emissions control	Extended studies in this area
Interest in aging results	Obtained hydrothermal and S aging results (studies ongoing)
Purge, lean-rich transitions, and transient control	Project moving more in this important direction
Modeling	Outside of project scope but collaborations with modeling community

added cost to a lean burn versus a stoichiometric GDI engine, **seems achievable**…running lean enhancements…**well focused on fuel economy targets**.

Funding: if more funds needed to shift some work into the engine approaches, money should be made available, at least enough to get data for a new proposal…**not sure why modeling had not been integrated into the tasks**

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Summary of Technical Accomplishments

- **Completed full characterization on bench flow reactor of Umicore prototype catalyst matrix**
  - Fixed load cycle vs. load step cycle results
  - Using more challenging HCs

Catalyst Sample Matrix [OSC=oxygen storage capacity; NSC=NOx storage capacity]

sample ID	Description	Pt (g/l)	Pd (g/l)	Rh (g/l)	OSC	NSC
Malibu-1	Front half of TWC	0	7.3	0	N	N
Malibu-2	Rear half of TWC	0	1.1	0.3	Y	N
Malibu-combo	Full TWC	0	4.0	0.16	Y	N
ORNL-1	Pt + Pd + Rh	2.47	4.17	0.05	Y	Y
ORNL-2	Pd + Rh	0	6.36	0.14	N	N
ORNL-6	Pd	0	6.50	0	N	N
ORNL-5	Pd + OSC high	0	6.50	0	H	N
ORNL-4	Pd + OSC med	0	4.06	0	M	N
ORNL-3	Pd + OSC low	0	1.41	0	L	N

- **Performed hydrothermal and S rapid aging of TWC (Malibu-1)**
  - Using industry approved cycle methodology (ongoing)
- **Preliminary results obtained from engine out NOx optimization studies**
  - Ongoing studies targeting minimizing rich period of lean-rich cycle
- **On engine studies of load step and lean-rich-lean transitions (ongoing)**
  - Focus toward transient operation; details not discussed in this presentation

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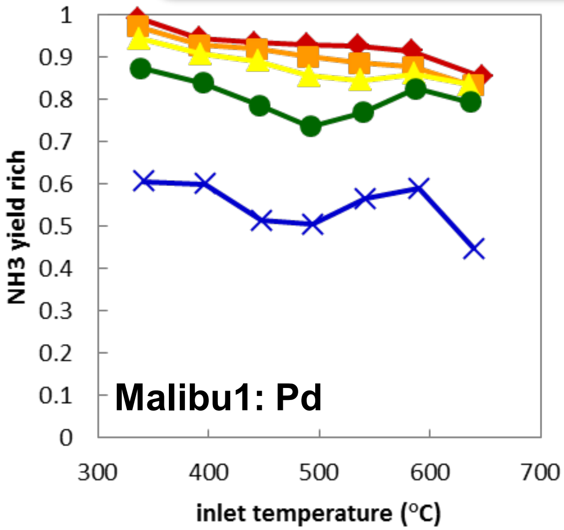
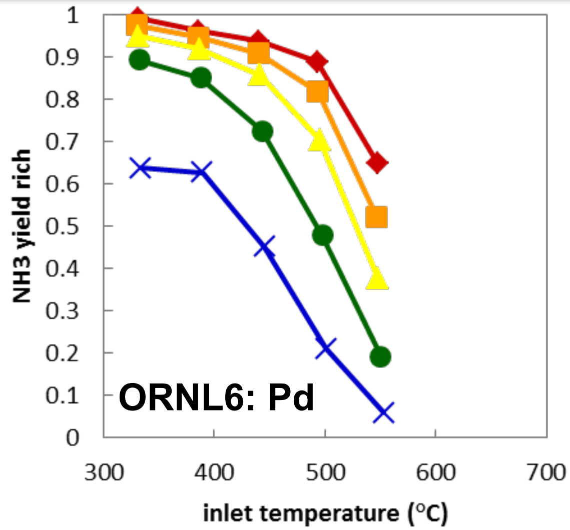
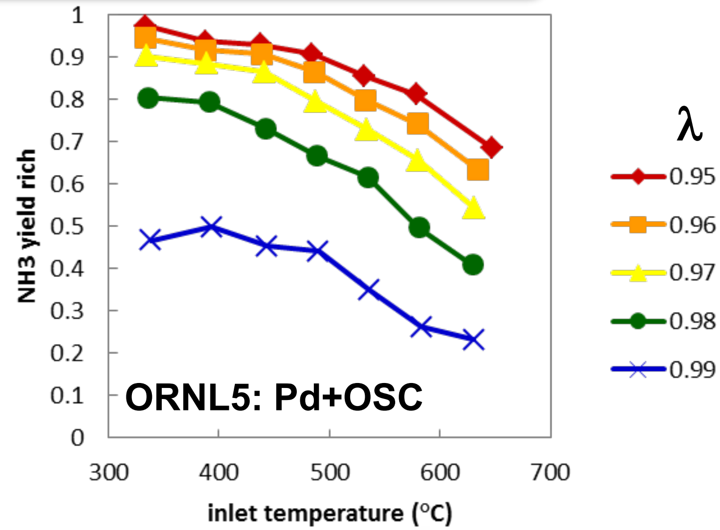
Bench Reactor Formulation Study: TWC formulation affects NH_3 yield during rich operation, particularly at high temperatures

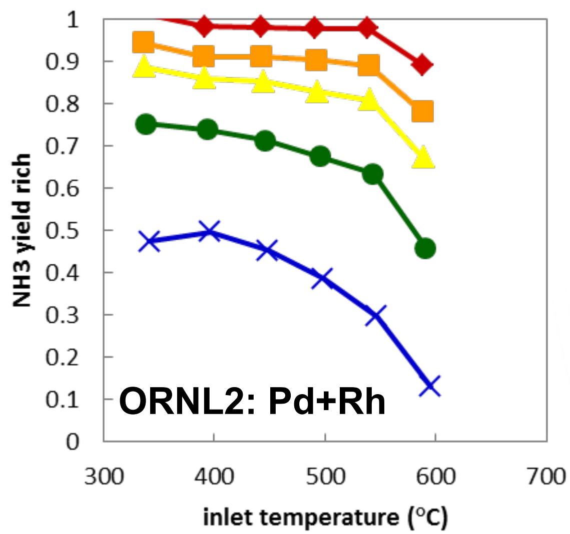
Results from fixed-load lean-rich cycles with feedback control based on NH_3:NOx [see backup slide 24 for full details]

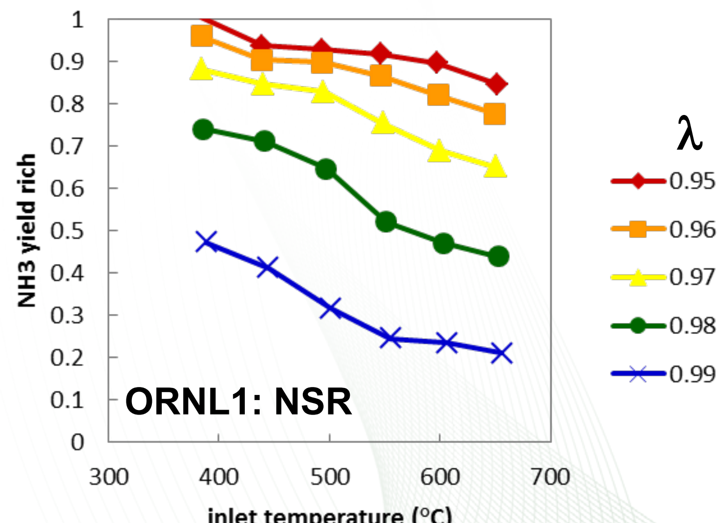






- Extensive data set: 5 formulations, 7 Ts, 5 λs, 2 conditions, 5 cycles
- Temperature, λ, TWC formulation all impact NH_3 selectivity
- Working to understand correlations between formulation & selectivity





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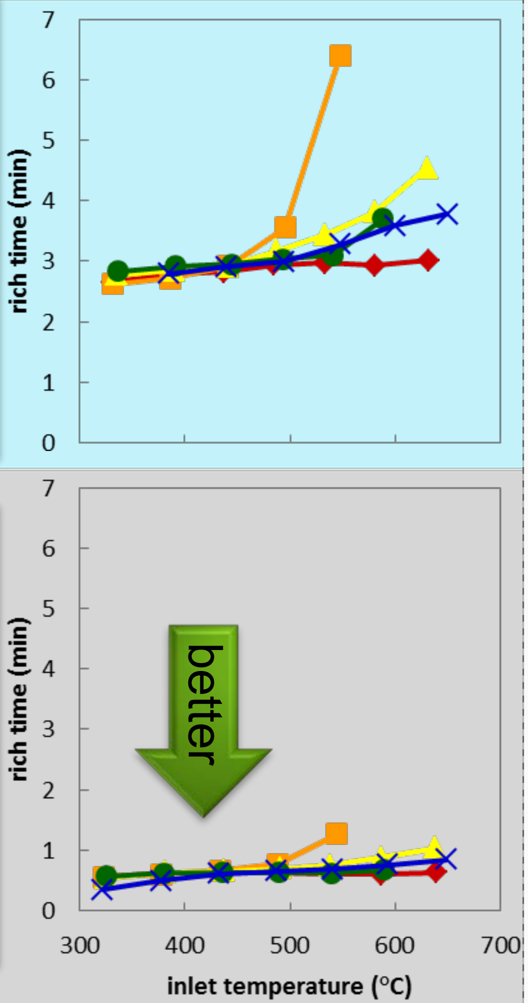
TWC formulation impacts fuel consumption through NH_3 selectivity (rich time) and NOx storage (lean time)

Rich Time (NH_3 selectivity)

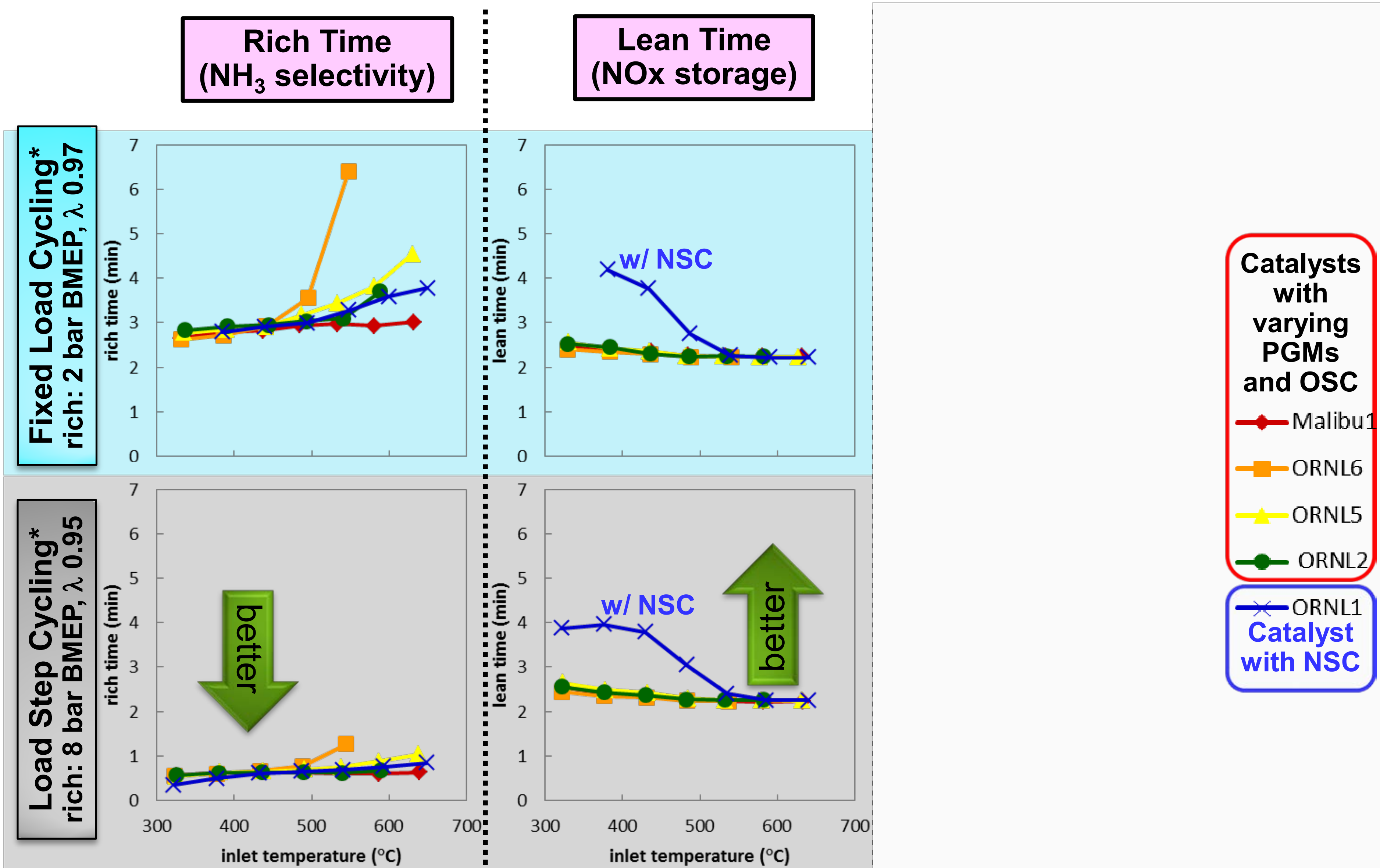
Fixed Load Cycling*
rich: 2 bar BMEP, λ 0.97

Load Step Cycling*
rich: 8 bar BMEP, λ 0.95



**Feedback controlled cycles (cycle average NH_3:NOx=1)*

TWC formulation impacts fuel consumption through NH_3 selectivity (rich time) and NOx storage (lean time)



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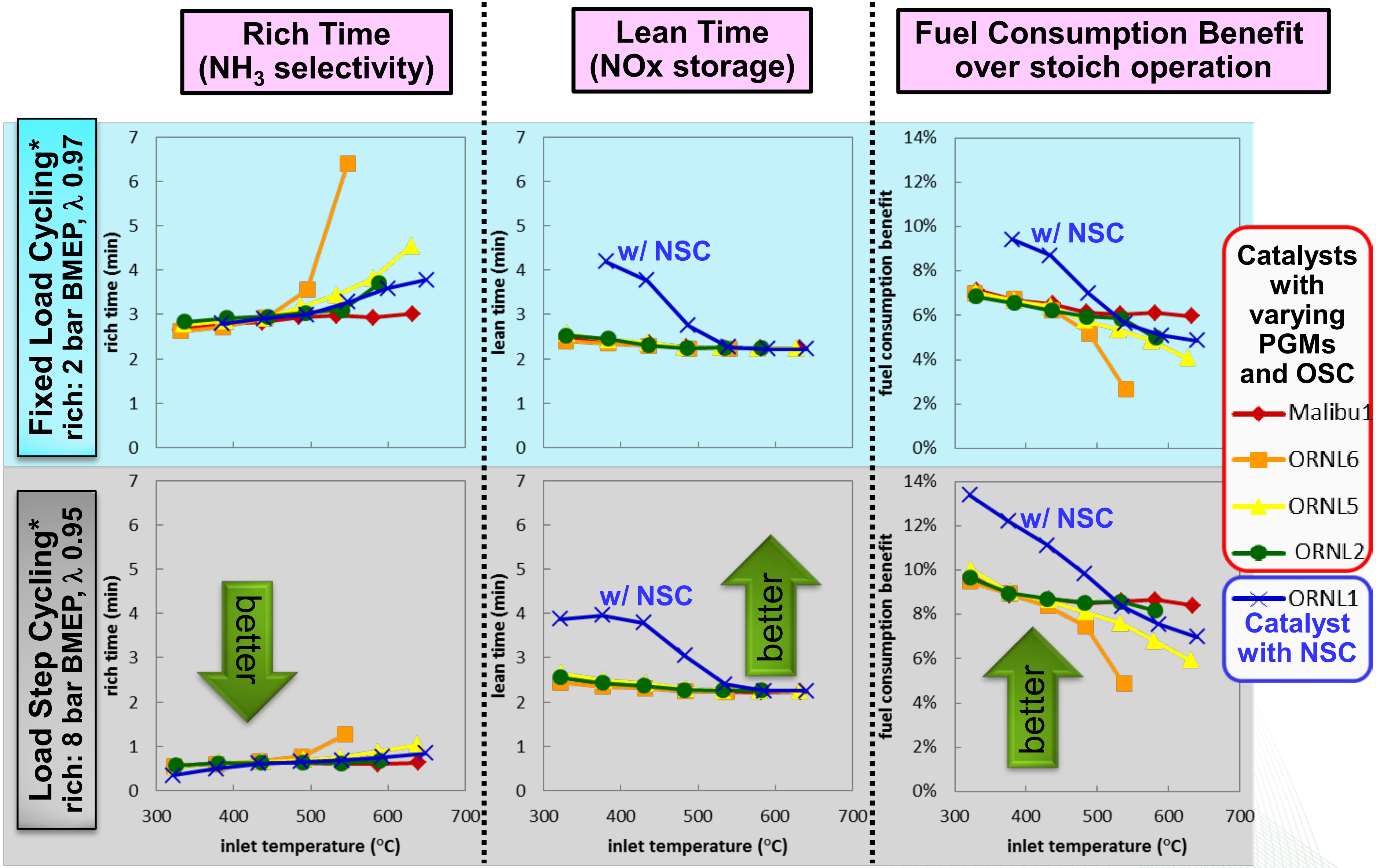

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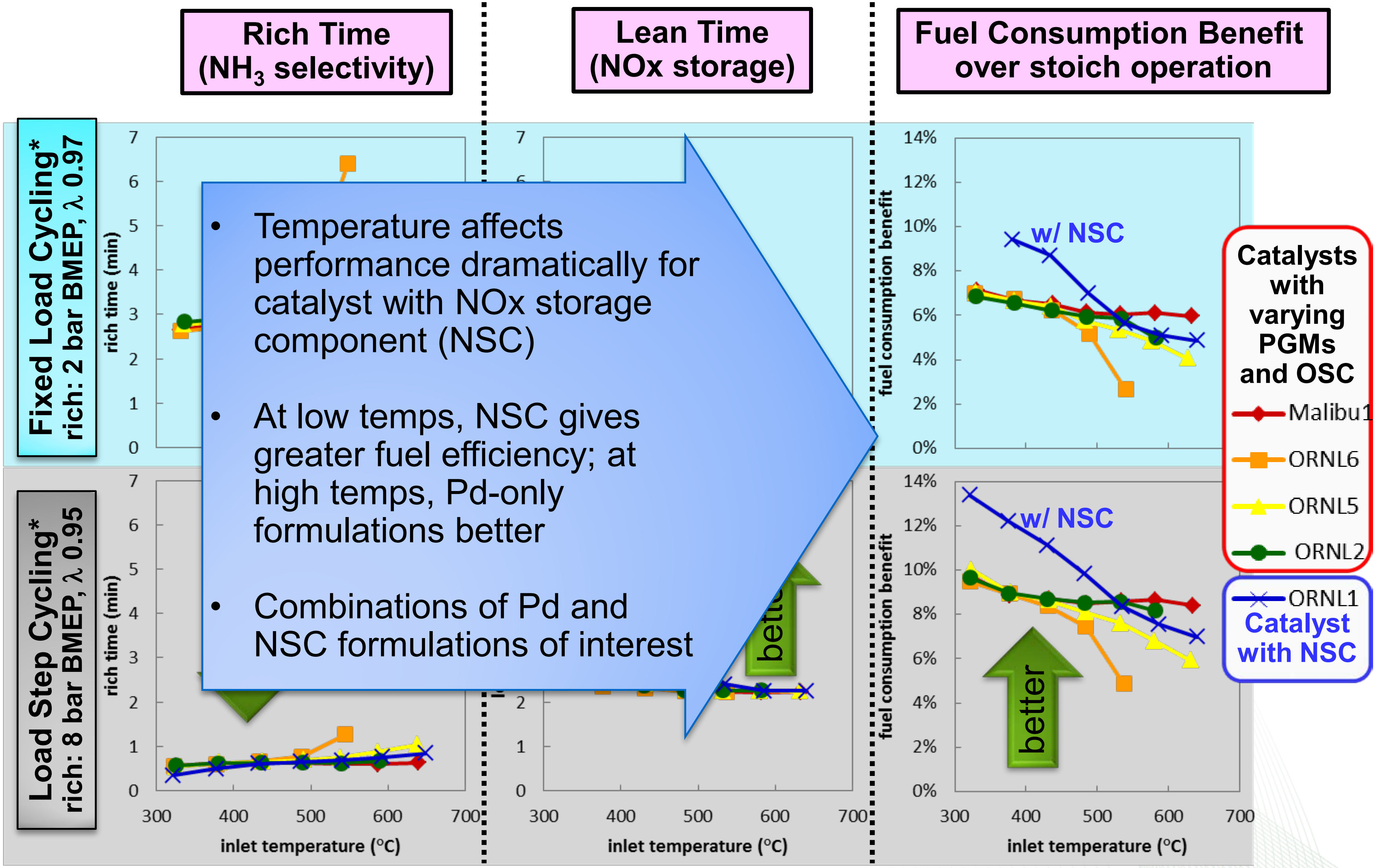
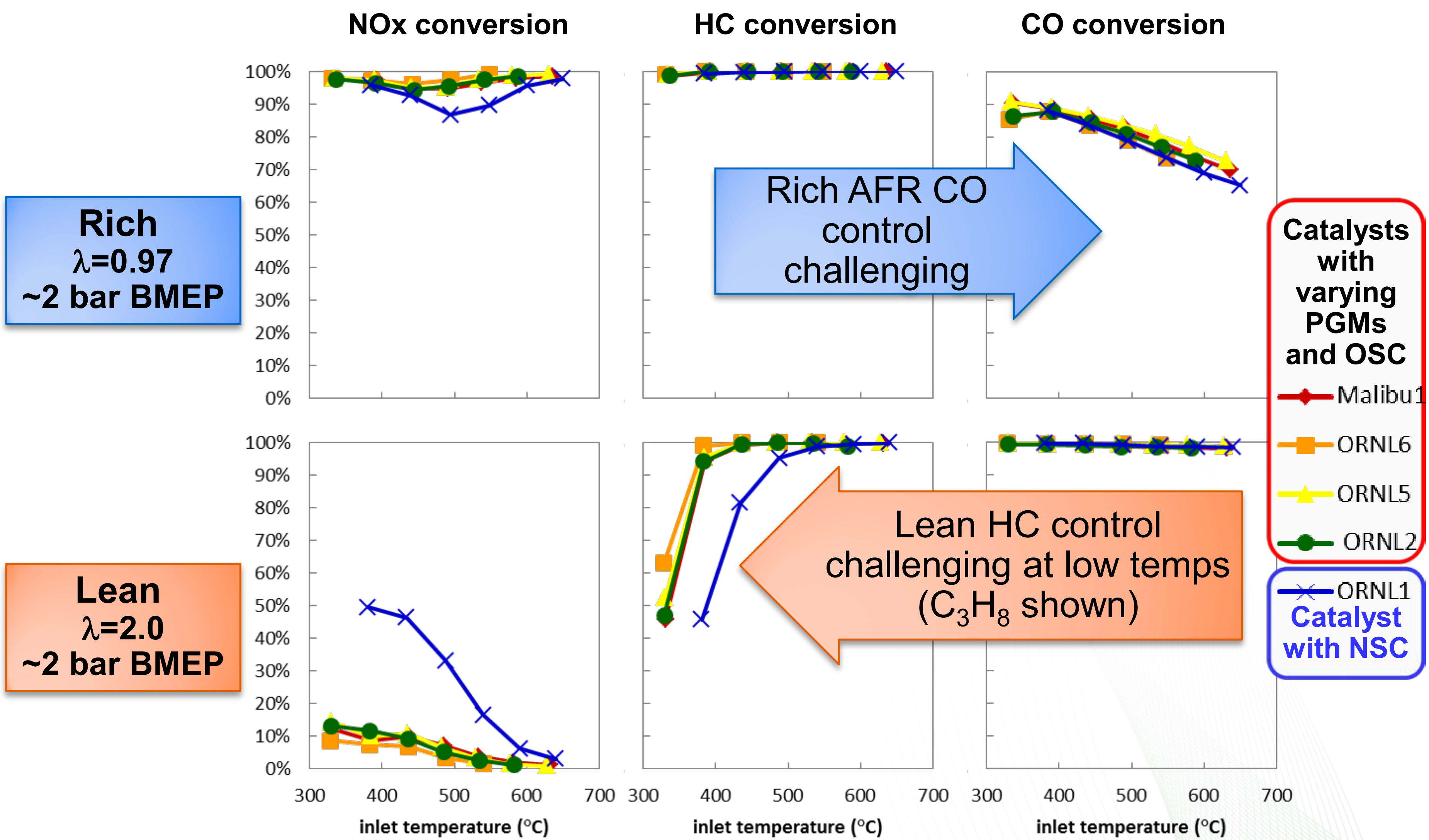


- Temperature affects performance dramatically for catalyst with NOx storage component (NSC)
- At low temps, NSC gives greater fuel efficiency; at high temps, Pd-only formulations better
- Combinations of Pd and NSC formulations of interest

Feedback controlled cycles (cycle average NH_3:NOx=1)

TWC conversions highlight remaining emissions challenges: lean HC, rich CO



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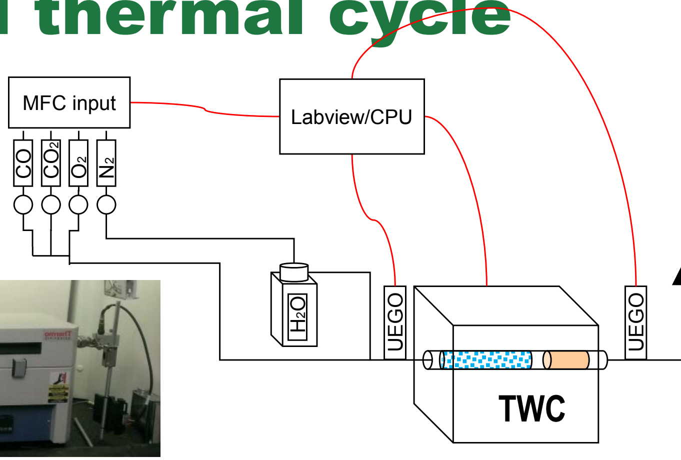
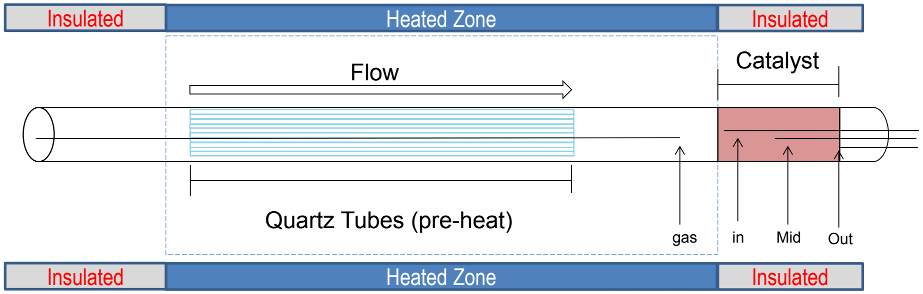
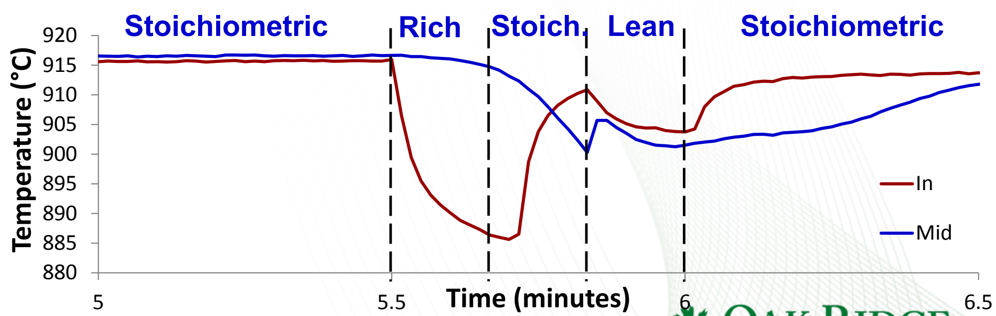
Aging and Poison Study: Dedicated thermal aging reactor built for industry-approved thermal cycle

- Automated aging with TWC located outside of heated zone
- Lean/Rich/Stoich. controlled through O_2 flow rate
- UEGO sensors before and after reactor to ensure proper cycling
- Thermocouple locations:
  - Gas inlet
  - Catalyst inlet/midbed/outlet
- Using UEGO and thermocouples, monitor as a function of aging:
  - Light-off, WGS, OSC
- Age TWCs to 25h, 50h, and 100h
- Post aging, evaluate fully in fully-functional bench reactor
  - Material characterization at USC





Phase 1	Phase 2	Phase 3	Phase 4
Stoich. 330s	Rich 10s	Stoich. 10s	Lean 10s



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High rich-phase NH_3 selectivity remains after thermal aging despite WGS reactivity deactivation

Experiment:

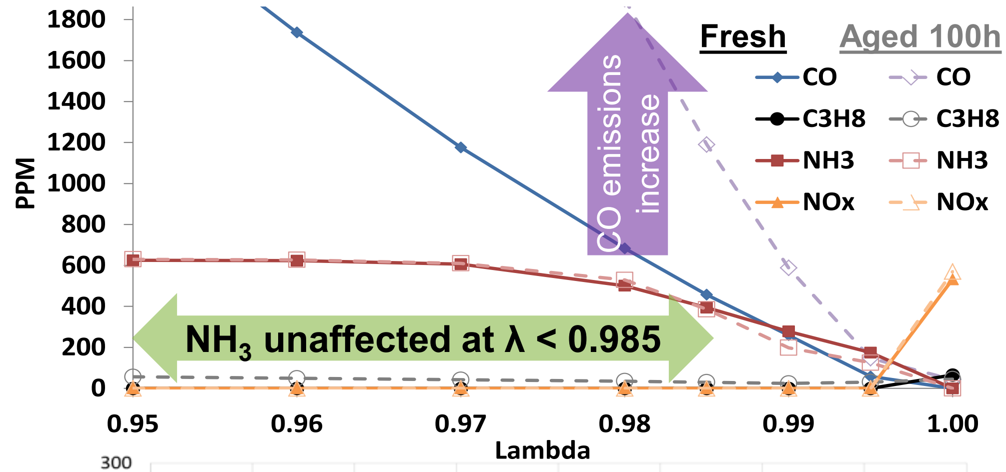
- Catalyst hydrothermally aged: Malibu-1 (Pd, no OSC)
- Aged 100 hours at 900°C (simulates lifetime)

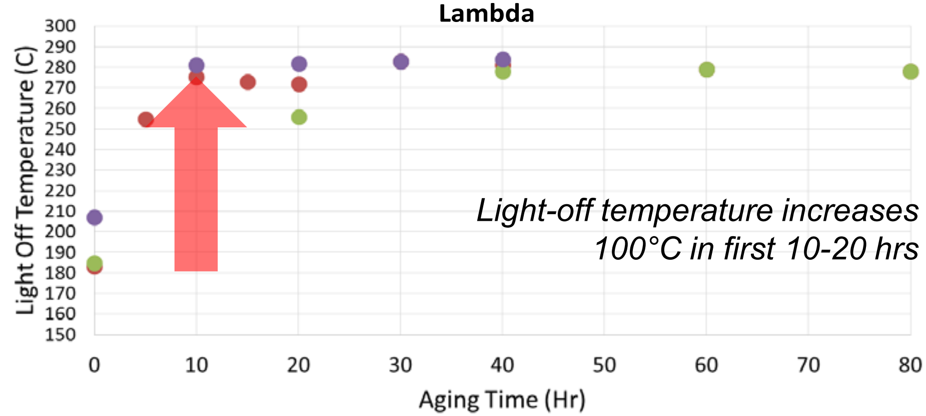
Minimally **Affected by Aging:**

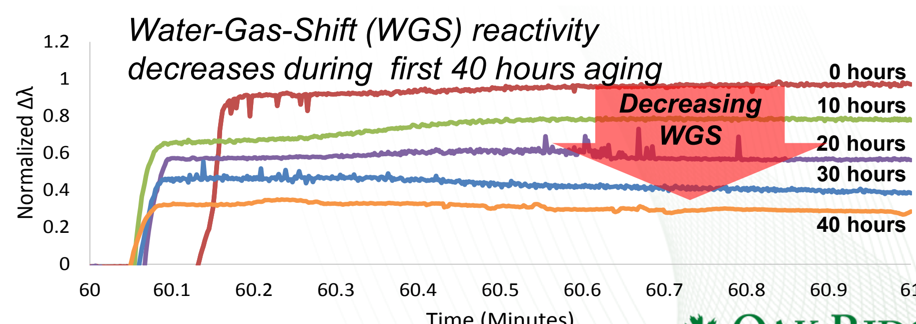
- NH_3 production
- HC slip
- OSC (at 500°C)

Significantly **Affected by Aging:**

- CO slip
- TWC light off temperature
- WGS reactivity







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Impact of sulfur exposure also evaluated for effects on passive SCR

Experiment:

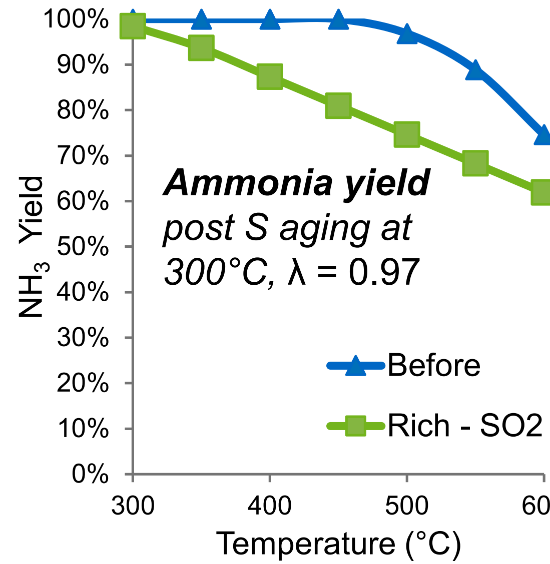
- Catalyst exposed to S: Malibu-1 (Pd, no OSC)
- Aged w/ 50 ppm SO_2 at 300°C for 4 hours under:
  - **Rich (λ=0.97)**
  - **Stoich (λ=1.00)**
  - **Lean (λ=2.00)**
- deS ramp to 600°C after S

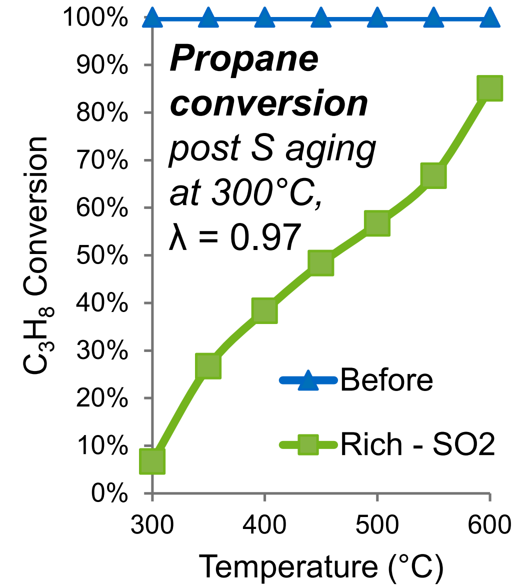
***Minimally* Affected by S:**

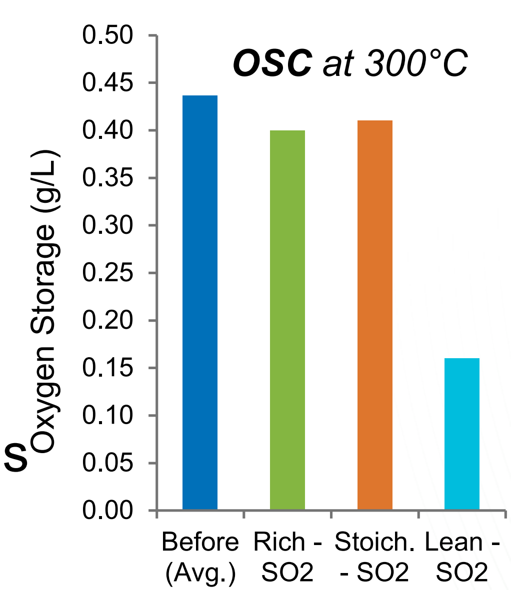
- NH_3 production
- OSC (at 300°C)

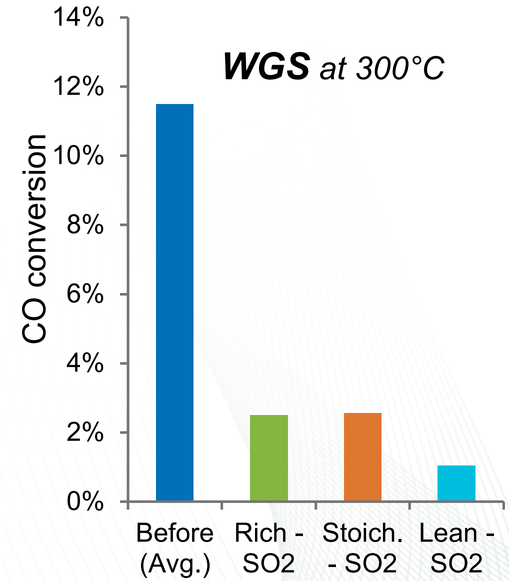
***Significantly* Affected by S:**

- HC slip during rich conditions
- WGS reactivity (at 300°C)









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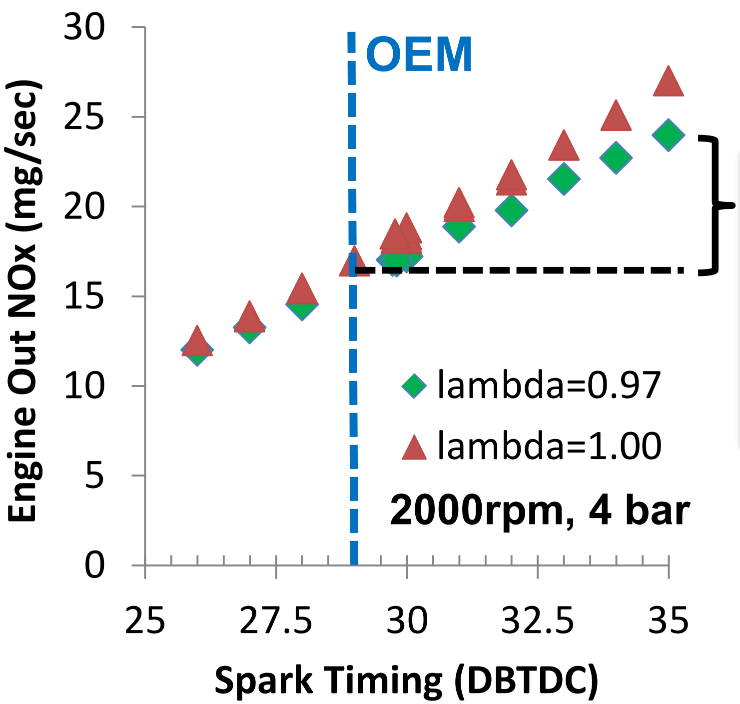
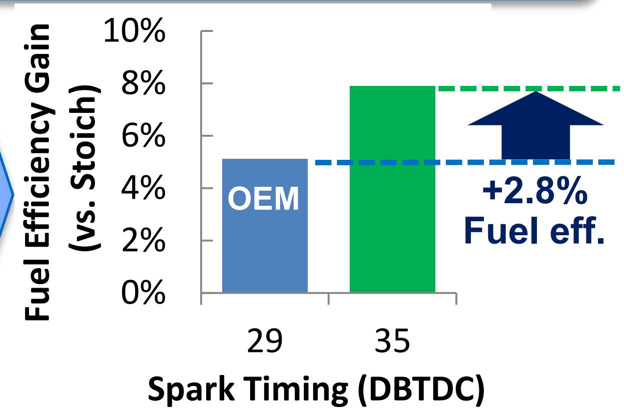
Adjusting rich spark timing can improve fuel efficiency (but not lean EGR)

Rich Period Spark Timing Adjustment: Goal is more NOx/NH_3

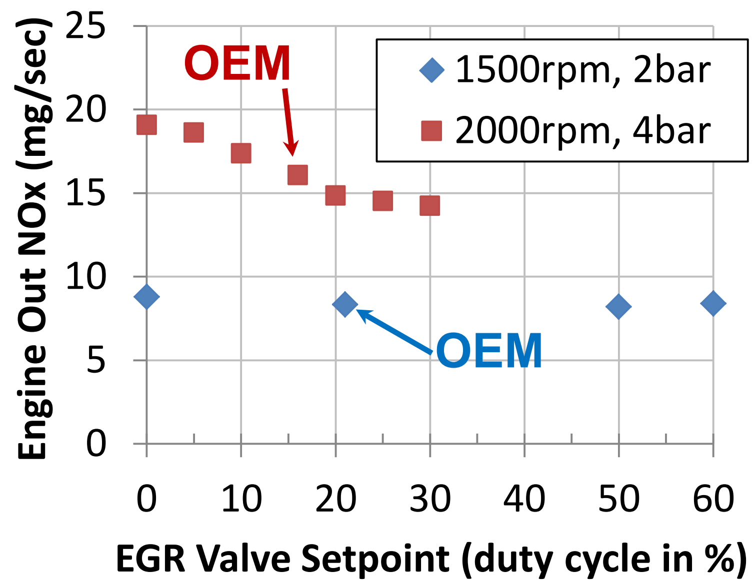


43% gain in Engine Out NOx = +2.8% gain in fuel efficiency*
(rel. to OEM point)



Lean Period EGR Adjustment: Goal is less NOx

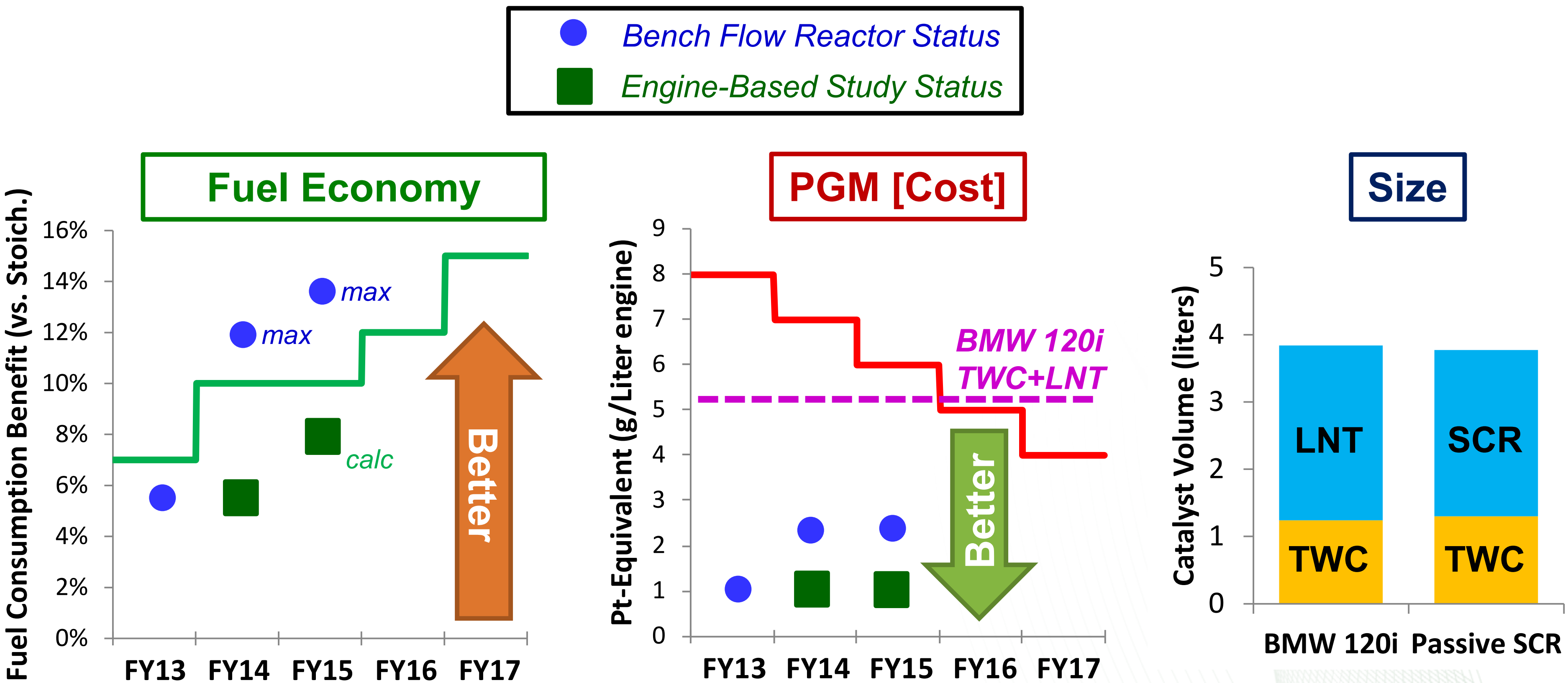
Investigated changing EGR level, but no significant effect observed (open throttle causes lack of dP to push EGR at low loads)



**calculated based on load step cycle and ideal SCR*

Remaining Challenges

- Improve system level fuel economy (reduce NH_3 production fuel penalty)
- Address catalyst performance during transients and rich-lean transitions
- Determine technique to enable NSC functionality over temperature range
- Broaden aging studies to include SCR



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Future Work: Addressing Remaining Challenges

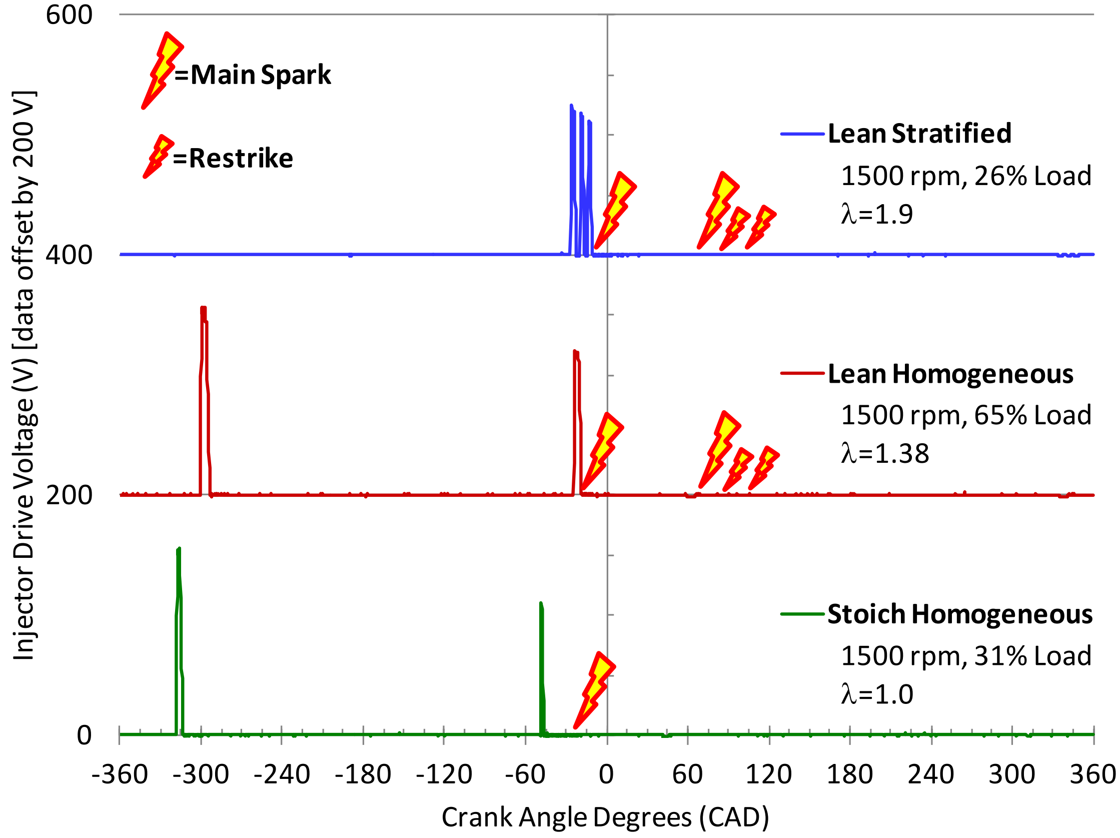
- Catalyst formulation studies on bench flow reactor
  - Revisit TWC+SCR with new information from prototype catalyst matrix
  - Combine Pd-based and NSC-containing TWCs to optimize
  - Examine SCR formulations for NH_3 oxidation
- Continue aging studies including studying select prototype formulations
  - Perform materials characterization (just starting) [TEM, BET/Chemi, XRD]
  - Continue aging of TWC formulations including with sulfur while cycling
  - Study aging of SCR
- Continue engine-based studies to maximize system fuel efficiency
  - Continue spark-timing studies for more efficient NH_3 production
  - Study select prototype TWC formulations on engine
  - Understand transient and switching effects on Passive SCR/LNT+SCR

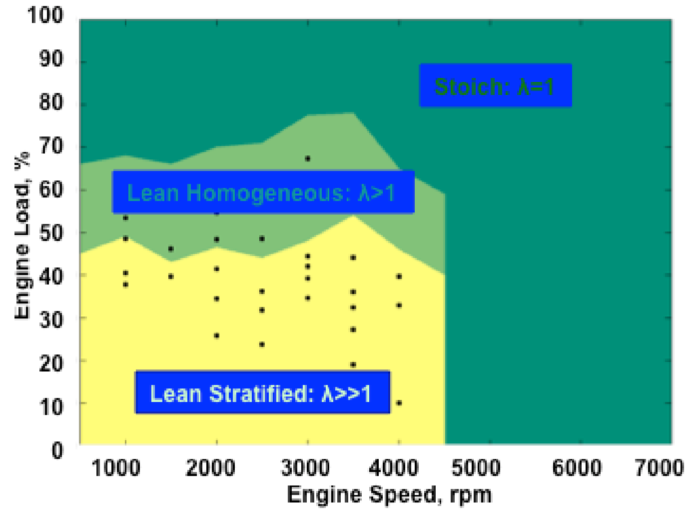
Summary

Relevance	Enabling lean gasoline vehicles will significantly reduce US petroleum use
Approach	Focus on non-urea Passive SCR and LNT+SCR
	Evaluate catalyst formulations on bench flow reactor for cost-effective emissions control
	Study fuel penalty and realistic performance on lean gasoline engine research platform
Collaborations	Industry: GM and catalyst suppliers Umicore and CDTi
	Universities: Univ. of South Carolina and the Univ. of Wisconsin
	National Labs: LANL (platform supported NH_3 sensor study)
Technical Accomplishments	**Completed full characterization on bench flow reactor of Umicore prototype catalyst matrix**
	Completed hydrothermal and S rapid aging of TWC (Malibu-1)
	Preliminary results obtained from engine out NOx optimization studies
Future Work	Bench reactor, aging, and engine studies ongoing toward 5-year project goals of fuel efficiency and cost (Pt-equivalent)

Technical Backup slides

BMW 120i engine features three main combustion modes





- Spray guided combustion system design
- Piezoelectric injectors operate at different voltages as well as different durations
- Multiple sparks enable ignition under lean operation
- In addition to three main combustions modes, there is also an OEM rich homogeneous mode for LNT control of NO_X emissions to meet EURO V NO_X emission standards

Catalysts Studied in Project

- Thanks to Umicore for supplying prototype catalysts (labelled ORNL-x)
- The Malibu catalyst is from an SULEV Chevrolet Malibu commercially available vehicle (represents existing state of the art)

sample ID	Description	Pt (g/l)	Pd (g/l)	Rh (g/l)	OSC	NSC
Malibu-1	Front half of TWC	0	7.3	0	N	N
Malibu-2	Rear half of TWC	0	1.1	0.3	Y	N
Malibu-combo	Full TWC	0	4.0	0.16	Y	N
ORNL-1	Pt + Pd + Rh	2.47	4.17	0.05	Y	Y
ORNL-2	Pd + Rh	0	6.36	0.14	N	N
ORNL-6	Pd	0	6.50	0	N	N
ORNL-5	Pd + OSC high	0	6.50	0	H	N
ORNL-4	Pd + OSC med	0	4.06	0	M	N
ORNL-3	Pd + OSC low	0	1.41	0	L	N

Note: OSC=oxygen storage capacity; NSC=NOx storage capacity

Conducted transient flow reactor experiments to estimate TWC effects on fuel consumption

- Used feedback-controlled cycles on flow reactor to evaluate dynamic TWC response in context of passive SCR
- Evaluated two different simulated engine cycles (fixed load, load step)

	fixed load		load step	
	rich	lean	rich	lean
load (BMEP)	2 bar	2 bar	8 bar	2 bar
SV (h^{-1})	**27000**	45000	**60000**	45000
NOx (ppm)	**600**	360	**1200**	360
max lean time	**50%**		**80%**	
simulates	cruise		"hill" transient	

	Rich						Lean
λ	0.95	0.96	0.97	0.98	0.99	1.00	2
O_2 (%)	0.96	1.02	1.07	1.13	1.17	1.22	10
CO (%)	2.0	1.8	1.6	1.4	1.2	1.0	0.2
H_2 (%)	1.0	0.9	0.8	0.7	0.6	0.5	0
NO (ppm)	600 (or 1200)						360
C_3H_8 (ppm C_1)	3000						1900
H_2O (%)	11						6.6
CO_2 (%)	11						6.6
TWC SV (hr^{-1})	27000 (or 60000)						45000

- Compositions & flows selected to mimic BMW GDI engine exhaust
- Space velocity changed with λ and load
- C_3H_8 chosen as challenging HC